



Short communication

An improved direct current sintering technique for proton conductor – $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$: The effect of direct current on sintering process



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HIGHLIGHTS

- An improved sintering technique called DC-sintering was developed for ceramics densification.
- Proton conductor of BZCYYb was densified at 850 °C within one hour by applying DC-sintering technique.
- The effect of current density and other parameters in DC-sintering have been studied.
- DC-sintering process has been reasonably explained by joule heating and black body radiation theory.

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ABSTRACT

$\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ (BZCYYb), a promising proton conductor of poor sinterability used in Solid Oxide Fuel Cells (SOFCs), has been densified in one hour at 850 °C by applying direct current sintering technique (DC-sintering). Under a constant electrical field, the current density through the specimen of BZCYYb rises rapidly when the temperature increases to a certain value. In DC-sintering process, we restrict the current density when the sharp increase occurs. By limiting current density to different values for one hour, we find that current density is the most important factor in DC-sintering process. The conductivity and the grain size of BZCYYb electrolyte increase significantly with the enhanced current density, while the different initial applied electrical fields have negligible effect. The stable stage of DC-sintering process can be explained by Joule heating. Corresponding real temperature of specimens is estimated by applying black body radiation theory.

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1. Introduction

Solid oxide fuel cells (SOFCs), an environmentally friendly energy transition system with high efficiency, have been widely considered as one of the best alternative technologies [1]. To acquire sufficient conductivity of electrolyte, however, the operating temperature for most SOFCs is usually between 800 °C and 1000 °C, which incurs not only the economic burden including the consumption of expensive materials and heating up energy but also long start-up time [2]. Therefore, there is a growing demand for the electrolyte which can meet the requirement of next generation of SOFCs operating at intermediate temperature (400 °C–700 °C).

High temperature proton conductors (HTPCs) are promising materials used as the electrolyte of SOFCs in last decade, which can provide higher ionic conductivity than that of most conventional oxygen-ion conducting electrolytes at low temperature because of their low activation energy for proton conduction [3]. Currently, doped BaCeO_3 and BaZrO_3 are two most attractive proton conductors [4–6]. Regrettably, both materials have drawbacks that cannot be disregarded. BaCeO_3 , in spite of its large proton conductivity, shows chemical instability in H_2O and CO_2 -containing atmospheres [7,8]. As for BaZrO_3 , although it possesses excellent stability, poor conductivity and refractory nature for sintering heavily restrict its application [5,6,9]. Recently, it is reported that $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ (BZCYYb), a co-doped barium zirconate-cerate with Y and Yb, combines the advantages of large proton conductivity and sufficiently high stability [10].

Although the sinterability of BZCYYb has been improved compared with BZY, conventional sintering temperature of 1550 °C

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and dwell times of 10 h are still necessary for BZCYYb to achieve relative density of 96% [10]. The conventional sintering process is not only time consuming, but also oppressively required of energy and equipment. Several alternative sintering methods have been proposed, such as adding sintering aids or wet chemical synthesis of nano-size powders. However, these methods either decrease the conductivity of the electrolyte [11] or have no important impact on densification process [12].

Recently, some novel techniques applying electrical fields in densification of ceramics have obvious improvement in terms of reducing the sintering temperature and the sintering time [13,14]. Among these techniques, flash-sintering is a promising technique for the densification of ceramic oxides [15]. By using this technique, densified of 8YSZ bulk which is a common electrolyte used in SOFCs can be obtained in a few seconds (less than 5 s) at 750 °C under an electrical field of 150 V cm⁻¹ [16]. Basically, flash-sintering is a process that by applying a proper electrical field the current increases sharply when the specimen is heated to a certain temperature. Only few seconds will be needed to achieve densification because of the surge of the current density. This electrical technique for densification provides us with an opportunity to accelerate the realization of next generation of SOFCs.

Many works about flash-sintering have been done by Raj and his coworkers [15–19]. And many oxygen-ion conductive ceramics have been densified by flash-sintering technique, including 3YSZ, 8YSZ, Co₂MnO₄ [15–17]. They also studied the effect of particle size in flash-sintering process and tried to interpret the phenomenon with Joule heating theory [18,19]. One of our previous works also studied the flash-sintering phenomenon in sintering GDC bulks, and it showed that the electrical field had obvious impact on grain size [20]. However, during these works, flash-sintering phenomena have only been observed in oxygen-ion conductors, such as YSZ and GDC, while the DC flash-sintering of protonic materials has not been studied yet. Moreover, as flash-sintering is an event marked by a sudden surge of current density in just a few seconds, the process is not controllable any more [18,19]. The steep rise of current density and the severe shrinkage of materials can even lead to structural fracture.

In this work, we applied direct current to promote densification of BZCYYb for the first time. To prevent the avalanche of current density in flash-sintering, an improved direct current sintering (DC-sintering) technique has been set up. We moderated the sintering rate by limiting the current density to a certain value and extend the sintering time from a few seconds to an hour. The effect of current density has been stressed in this paper. In addition, we studied the mechanism of DC-sintering process and presented an interpretation with Joule heating theory.

2. Experimental

2.1. Powder preparation

BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O₃ (BZCYYb) powders were prepared by sol–gel method, where citrate and ethylenediamine tetraacetic acid (EDTA) were employed as cooperating complexing agents. Ba(NO₃)₂, Zr(NO₃)₄·5H₂O, Ce(NO₃)₃·6H₂O, Y(NO₃)₃·6H₂O, Yb(NO₃)₃·5H₂O (all reagents are A.R.) were dissolved in distilled water at stoichiometric ratio. Then, citric acid and EDTA were introduced with the molar ratio of total metal ions to EDTA to citric acid set at 1:1:2. The pH value of the solution was adjusted to 6.0 with ammonia. After agitation for half an hour, the solution was put in a loft drier of 120 °C for 72 h to form a black gel. The gel was then calcined at 1000 °C for 5 h.

2.2. DC-sintering process

The prepared BZCYYb powder was mixed with 5-wt% PVA binder in aqueous solution. Then the mixture was uniaxially pressed into a bar-shaped die under a pressure of 500 MPa. The bar had a length of 20 mm and a rectangular cross section of 1.6 mm × 6.5 mm. The bar was bounded with the platinum wire at each end as electrodes. Platinum paste was coated on each end to make sure a good contact between the BZCYYb bar and the platinum wires, and to achieve a constant electrical field through the bar. The schematic is shown in Fig. 1. Sintering was performed in a tubular furnace under the application of a constant DC voltage with a heating rate of 10 °C min⁻¹. The power supply was switched to current control when the current reached a preset value. Then we maintained the state for one hour at 850 °C. Dividing current value by cross-sectional area which is 0.1 cm², we can calculate the corresponding current density. In this experiment, the current value is controlled to 0.1 A, 0.3 A, 0.5 A, 0.7 A, 0.9 A, respectively. Correspondingly, the current density is 1 A cm⁻¹, 3 A cm⁻¹, 5 A cm⁻¹, 7 A cm⁻¹, 9 A cm⁻¹. The applied electrical field is 60 V cm⁻¹, 70 V cm⁻¹, 80 V cm⁻¹, respectively.

2.3. Characterization

The phase compositions of BZCYYb powders were identified by X-ray diffraction (XRD) analysis on Rigaku D/max-2000 X-ray diffractometer with monochromatic Cu K α radiation (45 kV, 50 mA). The surface morphology of the DC-sintered specimens was characterized by scanning electron microscopy (SEM, Quanta FEG 250, FEI).

To obtain the bulk conductivity of sintered BZCYYb specimens, electrochemical impedance spectroscopy (EIS) was carried out by a potentiostat (PARSTAT M2273, Princeton Applied Research). The specimens were tested under the atmosphere of humidified hydrogen (3 vol% H₂O) at a flow rate of 50 mL min⁻¹. The frequency range applied was from 100 mHz to 2 MHz with a signal amplitude of 10 mV.

3. Results and discussion

3.1. X-ray diffraction analysis of BZCYYb powders

The room temperature X-ray diffraction pattern of BZCYYb powders is shown in Fig. 2. It can be observed that BZCYYb powders prepared by EDTA–citrate complexing sol–gel method are highly phase-pure perovskite. Compared with the standard diffraction pattern of BaCeO₃ (JCPDS Card No. 35-1318), no characteristic peaks from impurities are detected. Therefore, pure BZCYYb powders have been successfully synthesized by sol–gel method.

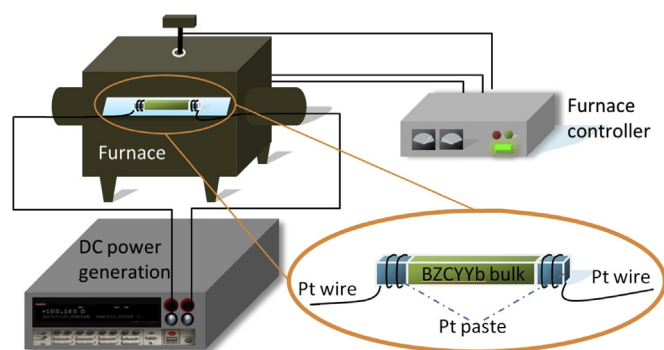


Fig. 1. Schematic of DC-sintering device.

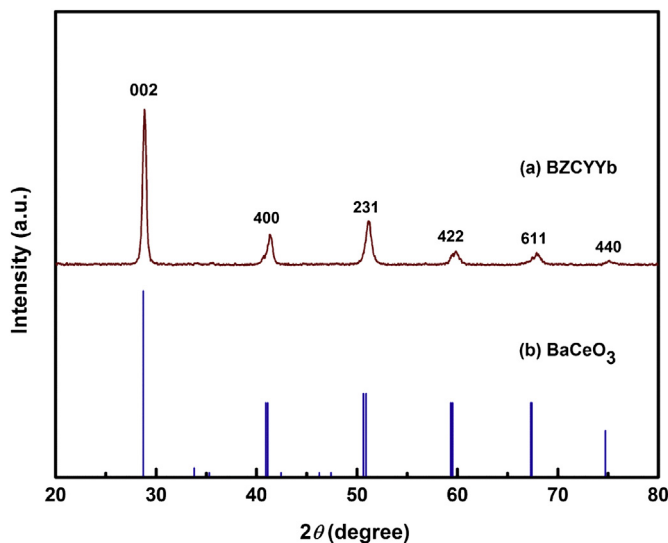


Fig. 2. (a) XRD pattern of BZCYYb powders prepared by sol–gel process. (b) Standard XRD pattern of BaCeO₃.

3.2. Effect of direct current density

As Fig. 3 records, the current density in BZCYYb bulk increases suddenly when the furnace's temperature reaches a certain value which is known as the onset of flash-sintering [15]. It is clear that the phenomenon of flash-sintering are observed in protonic materials as well as oxygen-ion conductive ceramics. And the onset temperature for the specimen under the field of 60 V cm⁻¹, 70 V cm⁻¹ and 80 V cm⁻¹ is 828 °C, 792 °C and 670 °C, respectively. The onset temperature decreases when the initial electrical field is enhanced. This result is consistent with previous reports [15,16,20]. Besides the electrical field, the onset temperature is also related to the very nature of material. The onset temperature for GDC is 545 °C [20] in contrast to 792 °C for BZCYYb under the field of 70 V cm⁻¹. This is due to the poor sinterability of BZCYYb. In order to investigate the effect of the current density on DC-sintering process, the current density is limited to a certain value (marked with the dash line in Fig. 3, 1 A cm⁻², 3 A cm⁻², 5 A cm⁻², 7 A cm⁻², 9 A cm⁻²) after the onset temperature under the initial field of

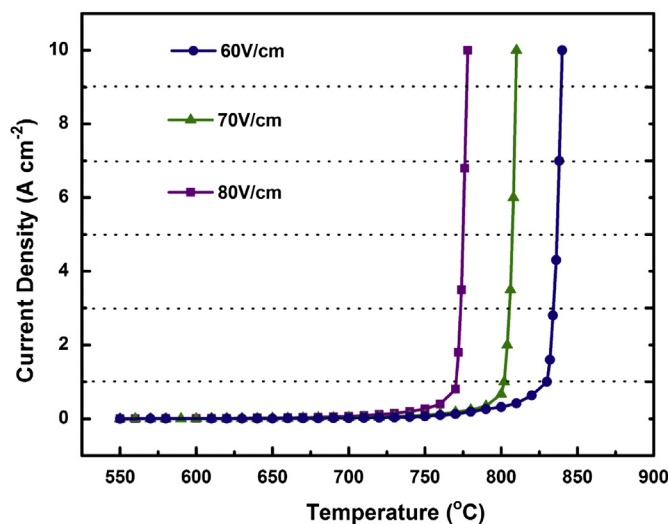


Fig. 3. Current density as a function of temperature in flash-sintering process.

70 V cm⁻¹. By holding on each current density for one hour, the BZCYYb bulks are sintered.

BZCYYb bulks sintered under different current densities are compared in terms of microstructure and conductivity. Fig. 4 shows the SEM surface micrographs of the sintered specimens. The bulk without applying any direct current mainly consists of raw particles and shows rather porous structure (Fig. 4a) because 850 °C is far below the densification temperature of BZCYYb. When the current density increases to 3 A cm⁻², BZCYYb particles begin to bond with each other and grain boundaries are formed at particle–particle junctions (Fig. 4c). Dramatically, as the current density rises to 5 A cm⁻², the SEM graph indicates a well-densified structure with only few pores (Fig. 4d). When the current density is enhanced to 7 A cm⁻² and 9 A cm⁻² (Fig. 4e and f), the SEM observations demonstrate that BZCYYb bulks are fully dense. And the micrographs also reveal an interesting finding that with the increase of current density in DC-sintering, the average grain size increases correspondingly and significantly. Evidently, current density plays a dominating role in DC-sintering.

The dramatic change in grain size and densification with current density can be attributed to Joule heating at grain boundaries because we believe electrical energy can be converted to thermal energy and a current density corresponds to a real sintering temperature of BZCYYb bulks. Detail explanation will be discussed later.

Fig. 5 reports the EIS data of specimen sintered with the current density of 7 A cm⁻² under the initial field of 70 V cm⁻¹. All the spectra are actually comprised of two arcs. The arc at high and intermediate frequency area has an intercept with X axis, which represents the bulk total resistance (R_1) including grain interior resistance and grain boundary resistance [21,22]. The arc at low frequency corresponds to the interfacial resistance (R_2) including ion and electron transfer at the sample surface contacting the electrode [21]. The low frequency arc gradually shifts to high frequency area and changes to a semicircle from 400 °C to 800 °C, indicating the R_2 diminishes. This is because the electrode process accelerates with the increasing temperature.

The total conductivity of BZCYYb bulk can be determined based on the R_1 value obtained from Fig. 5. The conductivity is calculated according to the following equation.

$$\sigma = L/(RS) \quad (1)$$

where L is the distance between two platinum electrodes, and S is the cross sectional area.

Fig. 6 presents the conductivity of DC-sintered BZCYYb with different current density. From this comparison, it is clear that the increasing current density in DC-sintering process precipitates an increase in BZCYYb conductivity. Fig. 7 reveals the average grain size and the conductivity of DC-sintered BZCYYb as functions of the current density. As we can see, both curves show the near linear relationship with the current density. At the temperature of 800 °C, the bulks sintered with the current density of 1 A cm⁻² possess a conductivity of 3.6 mS cm⁻¹. When the current density increases to 9 A cm⁻², however, the conductivity is improved to 49.0 mS cm⁻¹. This conductivity implies that the DC-sintered BZCYYb bulk is a viable proton conducting electrolyte [10]. The average grain size of BZCYYb bulk increases from 0.15 μm to 0.9 μm when current density is adjusted from 1 A cm⁻²–9 A cm⁻². The average grain size is estimated by linear intercept method.

From Fig. 7, a conclusion can be drawn that BZCYYb bulk of larger grain size possess higher conductivity. Similar results have been covered [22]. It is reported that the bulk conductivity or interior grain conductivity in proton conductors is much higher than of grain boundaries. Thus, the resistance of grain boundaries contribute the main resistances of BZCYYb bulk. Consequently,

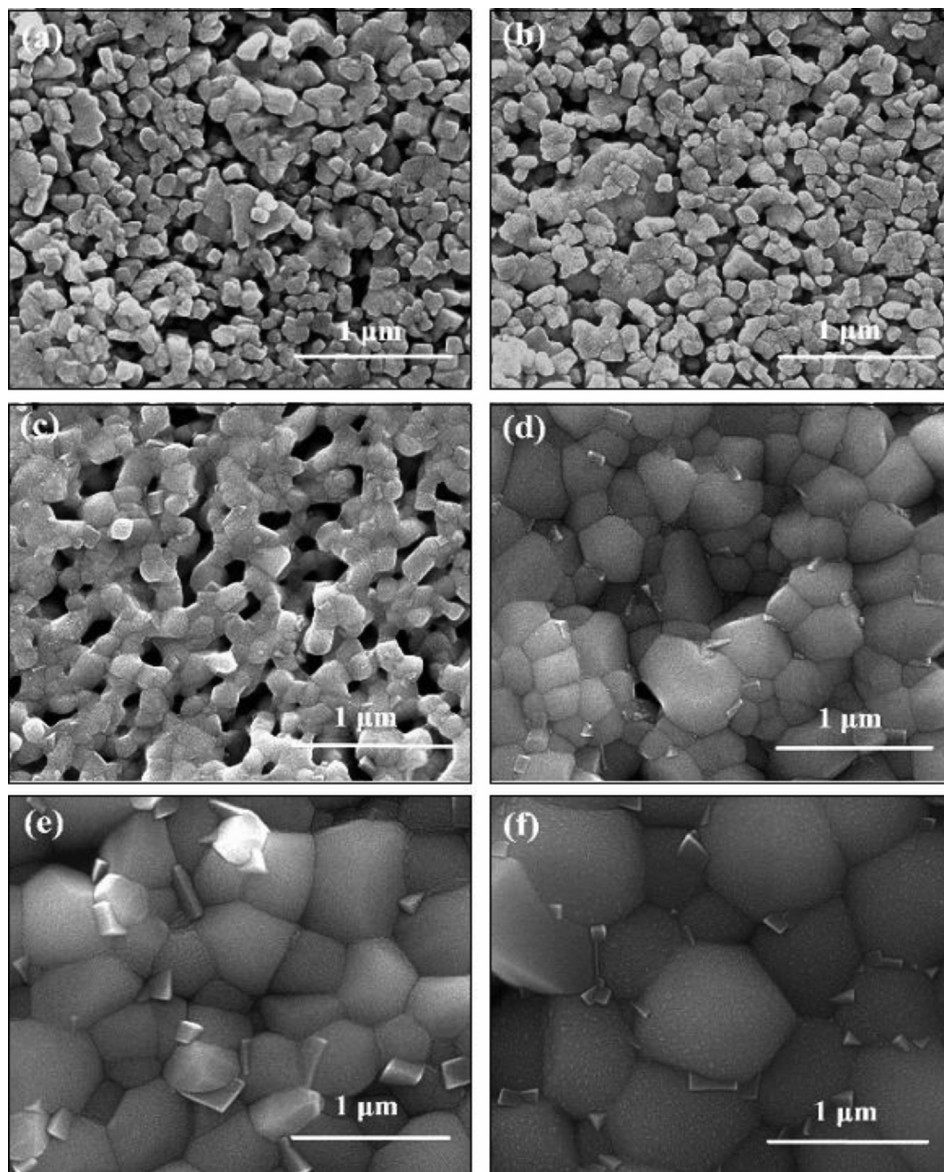


Fig. 4. Scanning electron micrographs of the surface of specimens sintered with different current densities. (a) No current applied, (b) 1 A cm^{-2} , (c) 3 A cm^{-2} , (d) 5 A cm^{-2} , (e) 7 A cm^{-2} , (f) 9 A cm^{-2} .

bulks with larger average grain size have larger proportion of grain boundaries, and they possess higher conductivity.

3.3. Effect of applied field

To study the effect of electrical field in DC-sintering, an experiment concerning about field of 60 V cm^{-1} , 70 V cm^{-1} and 80 V cm^{-1} , has been conducted. During this experiment, the limiting current density is 7 A cm^{-2} , and the dwell time is one hour.

SEM surface micrographs in Fig. 8 prove that there is no apparent reduction in grain size when increasing electrical field. The average grain size is about $0.6 \mu\text{m}$ for all three specimens. Fig. 9 shows the conductivity and the average grain size as functions of applied field. Three specimens are of the same level no matter in grain size or conductivity. The insignificant difference is caused by inevitable experimental errors, such as equipment errors in adjusting voltage and current.

Interestingly, in our experiment, applied field can only shift the onset of flash-sintering, while it has no effect on grain growth or

the conductivity of BZCYYb bulk. This result contradicts some previous findings [20,23,24] that believe applied voltage can restrict grain growth. This phenomenon can be explained by Joule heating theory in next section.

3.4. DC-sintering process explained by Joule heating

The phenomenon of flash-sintering can be explained by Joule heating theory, though some previous researches point out that the estimated temperature by this theory is far below the temperature that would be required to sinter the specimen in a few seconds [18,19]. However, it is important to note that the presumption of the theory is that the system is in thermal equilibrium. It is unconvincing to apply this theory during the first few seconds in flash-sintering, because system is not in equilibrium yet. Therefore, based on our observation when the current control sintering stage is stable, we still believe Joule heating by power dissipation and black body radiation is probably the most appropriate theory in this case.

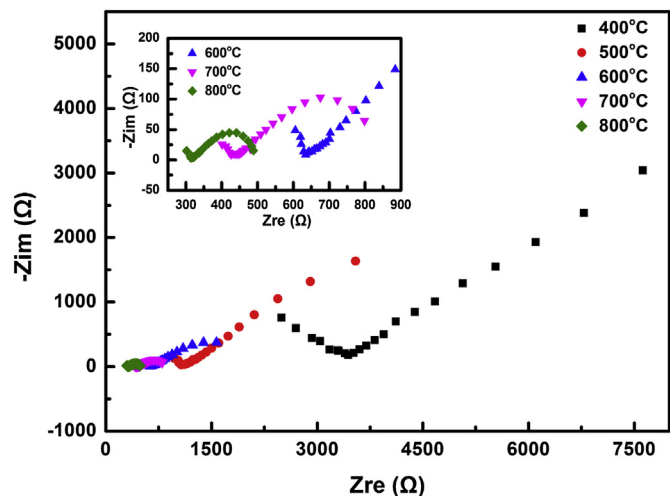


Fig. 5. EIS of the specimen sintered with the current density of 7 A cm^{-2} under the initial field of 70 V cm^{-1} .

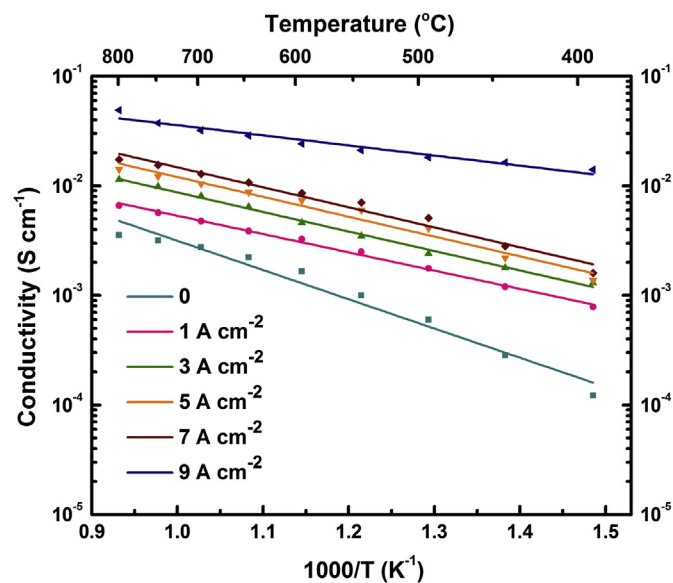


Fig. 6. Total conductivity (determined by EIS) of specimens sintered with different current densities.

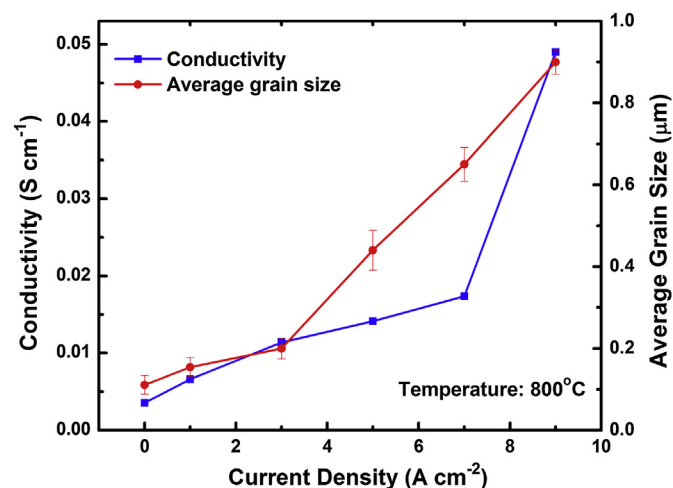


Fig. 7. Total conductivity determined by EIS and average grain size as functions of current density at 800°C .

When applying an electrical field to a specimen in a furnace, the specimen is heated not only by the furnace, but also by electrical power. Thus, the temperature is different between specimen and furnace. The difference can be estimated by an equation [Eq. (2)] that balances the power dissipation and black body radiation [18].

$$j^* + \frac{\Delta W}{A} = \sigma(T_0 + \Delta T)^4 \quad (2)$$

In this equation, T_0 (1123.15 K) is the temperature of the furnace. ΔT is the temperature difference between specimen and furnace. ΔW is the power supplied by electrical energy. A is the total surface

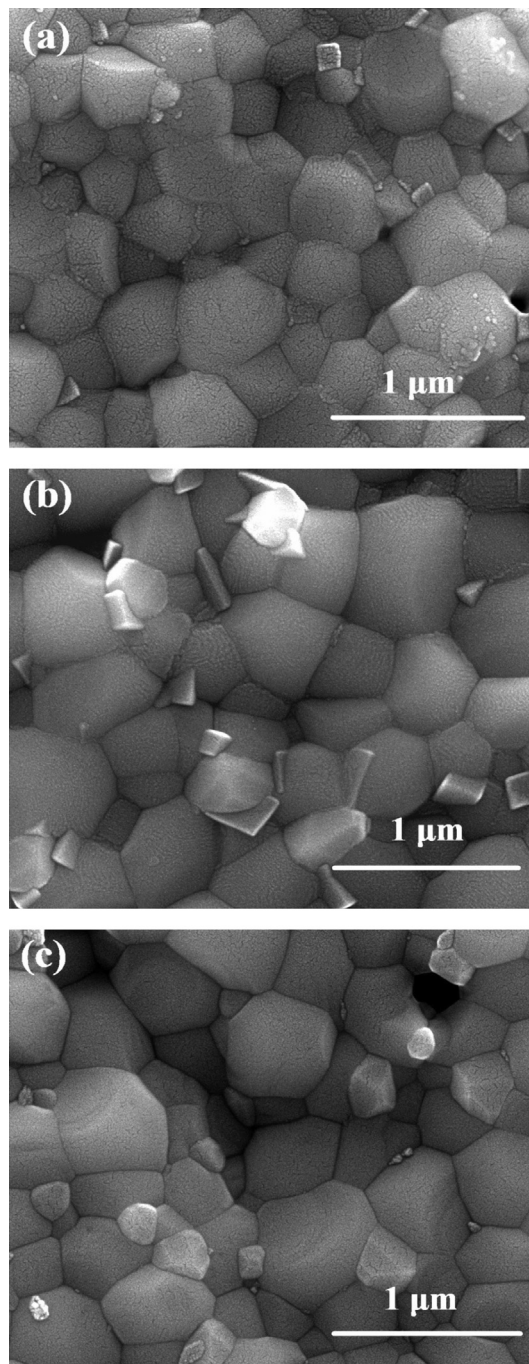


Fig. 8. Scanning electron micrographs of the surface of the specimens sintered with different initial electrical field. (a) 60 V cm^{-1} , (b) 70 V cm^{-1} , (c) 80 V cm^{-1} .

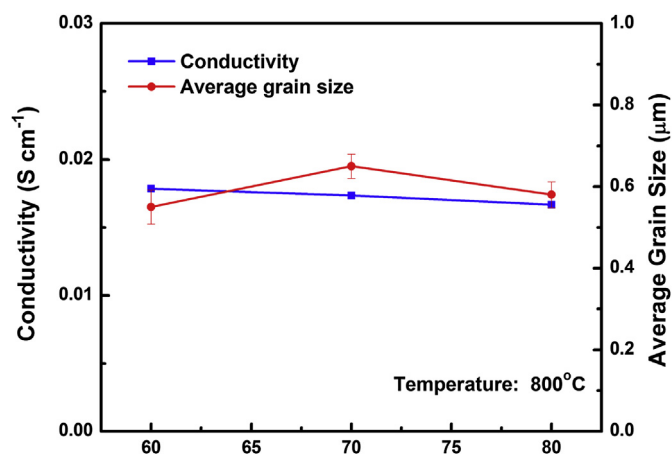


Fig. 9. Total conductivity determined by EIS and average grain size as functions of applied electrical field at 800 °C.

area of the specimen. In our experiment, $A = 2.888 \times 10^{-4} \text{ m}^2$, σ is the black body radiation constant equal to $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. j^* is the radiated energy from the specimen, which can be expressed by the Stefan–Boltzmann law, $j^* = \sigma T^4$. Substitute all the unknowns, we obtain the value of ΔT , then, the real temperature of specimen, T , is acquired. The results are reported in Table 1 and Fig. 10. It can be seen that as the current density rises, corresponding power dissipation increases. Consequently, the estimated temperature increases. Take the current density of 9 A cm^{-2} as an example, the estimated temperature of BZCYYb bulk is 1356.88 °C . This temperature is close to the densification temperature of BZCYYb synthesized by wet chemical route [12]. Notably, the estimated temperature refers to the specimen in thermal equilibrium condition, and the temperature of initial stage of DC-sintering process can even be higher.

Although the fundamental understanding of the mechanism is deficient, it is still reasonable to interpret flash-sintering behavior with a chain reaction mechanism [13]. During constant voltage period, when the temperature rises, grain growth process of BZCYYb bulks starts. Consequently, the conductivity of BZCYYb ceramic is magnified exponentially implying that the current is growing exponentially. Since the voltage is constant, the power supply is increasing with the current density. We can deduce a rise in temperature if we apply the black body radiation theory though it seems not precise on this condition. And the increased temperature, in turn, promotes the conductivity. This is the so-called chain reaction mechanism. Thus, flash-sintering occurs, as shown in Fig. 3.

However, in this work, to prevent the sudden increase of current density which may lead to structural fracture of BZCYYb bulk, the power supply was switched to current control after the onset of flash-sintering. At the very beginning of the current control period, the voltage applied to BZCYYb decreases substantially because of the sharp increasing of conductivity. And the real temperature of

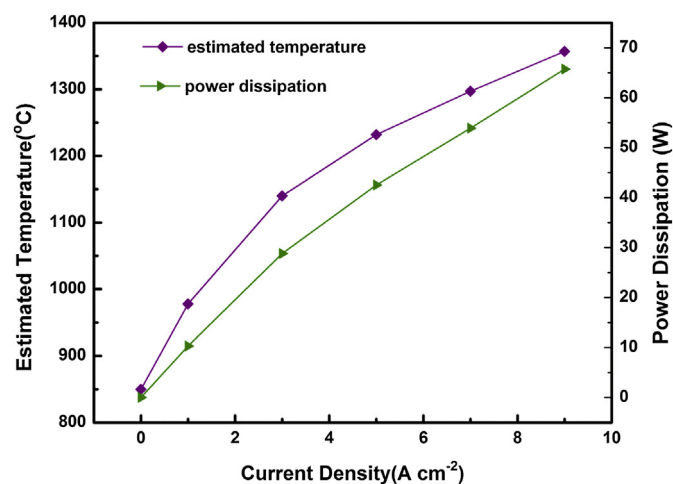


Fig. 10. Estimated temperature and power dissipation as functions of current density.

BZCYYb bulks can be far higher than we have estimated in Table 1. With the progress of sintering, there is a significant deceleration in the increasing rate of conductivity of BZCYYb. And the conductivity finally trends towards a constant value, whatever the initial field is, as shown in Fig. 9. Therefore sintering rate is relatively stable when restricting current in DC-sintering. In addition, by referring to Table 1, we can readily modulate actual temperature in specimen by controlling the value of current.

Finally, it is worth mentioning that the DC-sintering rate of the current control period is more stable than that of flash-sintering, and faster than that of conventional sintering process. And DC-sintering is also different from field assisted sintering in which the rate of sintering is gradually enhanced without reaching the onset of flash-sintering [25]. DC-sintering technique provides us with a way to achieve full control of the sintering process, and it is supposed to be also practical in other ionic conductive ceramics.

4. Conclusions

For the first time, BZCYYb bulk is densified at 850 °C in one hour by applying an improved direct current sintering technique (DC-sintering). Both the grain size and the conductivity of BZCYYb bulk increase with the rising current density, which implies the dominating role of current density in DC-sintering process. Meanwhile, the effect of electrical field is negligible on densification except shifting the flash-sintering point. And the DC-sintering process can be well explained by Joule heating. DC-sintering is a most attractive technology for promoting densification of oxide ceramic, in contrast to conventional sintering which requires relatively high temperature and long dwell time. Furthermore, by adjusting the current density and dwell time, the BZCYYb bulk with designed grain size can be obtained.

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Table 1
Some variables for different current densities.

Current density (A cm^{-2})	Initial voltage (V)	Voltage in stable condition (V)	Power dissipation (W)	Estimated temperature ($^{\circ}\text{C}$)
0	0	0	0	850
1	140	103	10.3	978
3	140	96	28.8	1140
5	140	85	42.5	1232
7	140	77	53.9	1297
9	140	73	65.7	1357

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